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U.S. Army Environmental Center

PHYTOREMEDIATION OF EXPLOSIVES CONTAMINATED GROUNDWATER IN CONSTRUCTED WETLANDS: I - BATCH STUDY

Prepared for
U.S. ARMY ENVIRONMENTAL CENTER
Aberdeen Proving Ground, Maryland 21010-5401

Funded Through

U.S. Department of Defense Environmental Security Technology Certification Program

Prepared by
Tennessee Valley Authority
Environmental Research Center
Muscle Shoals, Alabama 35660-1010

June 1995

TVA Contract No. TV-88826V
Report No. SFIM-AEC-ET-CR-96166

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Environmental Technology Division
Aberdeen Proving Ground, MD 21010-5401
POC: Ms. Darlene Bader

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The study evaluates the utility of constructed wetlands for remediating constructed wetlands using bench scale wetlands (batch type). Specifically the study examines: the degradation of TNT and RDX in contaminated waters in a variety of wetland types; the impact of wetland type on chemical oxygen demand; and tracks the level of degradation products in various wetland types. The study also provides design recommendations for the wetlands demonstration project to be located at the Milan Army Ammunition Plant (MAAP), in Tennessee.

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ABBREVIATIONS

2A-DNT	-2-Aminodinitrotoluene
4A-DNT	-4-Aminodinitrotoluene
°C	-Degrees Centigrade
Ca	-Calcium
COD	-Chemical Oxygen Demand
d	-Days
DNT	-Dinitrotoluene
DO	-Dissolved Oxygen
DoD	-Department of Defense
g/L	-Grams per liter
HPLC	-High Performance Liquid Chromatography
L	-Liters
MAAP	-Milan Army Ammunition Plant
mg/L	-Milligrams per liter
mL/min	-Milliliter per minute
mS/cm	-Millisiemens per centimeter
mV	-Millivolt
N	-Nitrogen
P	-Phosphorus
RDX	-Hexahydro-1,3,5-trinitro-1,3,5-triazine
TNT	-2,4,6 Trinitrotoluene
TVA	-Tennessee Valley Authority
U.S.	-United States
USAEC	-United States Army Environmental Center

Tab for Section 1.0

SECTION 1.0

INTRODUCTION

Wetland systems have been successfully used to treat a wide variety of wastewaters. Municipal wastewater and acid mine drainage encompass most of the water treated by constructed wetlands. Other wastewaters treated with wetlands include petroleum industrial effluents, pulp and paper wastewater, and landfill leachates. The main advantage of constructed wetlands is that the technology is inexpensive compared to conventional treatment options. There are capital costs associated with building the wetland, but the low operation and maintenance costs makes constructed wetlands a cheaper alternative to conventional treatments with yearly labor and chemical costs.

This study was conducted to determine the feasibility of using parrot feather in gravel bed and ponded wetland systems for treating TNT and RDX in contaminated groundwater by batch loading groundwater into small-scale wetland systems.

Tab for Section 2.0

SECTION 2.0

MATERIALS AND METHODS

The study was conducted from June 12 to 23. The experimental units consisted of 10 gallon aquaria that were separated into two equal compartments with a plastic partition. The aquaria were separated to allow for reciprocation of water in some of the treatments. An outline of the 10 treatments and 2 controls used in the study are summarized in Table 2-1.

Before adding the contaminated groundwater, the wetland reactors were allowed to acclimate with dechlorinated tap water with or without nutrients, depending on the nutrient treatment. The acclimation period lasted 5 days from June 6 to June 12. On June 12, 12 L of contaminated groundwater from the Milan Army Ammunition Plant (MAAP) was batch-fed into the wetland reactors. Water was recirculated in the systems at 50 mL/min. The groundwater contained 2.14 and 2.76 mg/L of TNT and RDX, respectively.

The 8 treatments with gravel consisted of all combinations of with or without plants, dirty or clean rocks, and with or without water reciprocation. Each treatment was replicated 2 times. The plant used in the study was parrot feather (*Myriophyllum braziliense*) planted as a submergent at a density of 50 g/L. The dirty and clean rocks treatment refers to the addition of inoculated rocks or non-inoculated rocks, respectively. Carbon was added to the contaminated groundwater with inoculated rocks. The groundwater was added without carbon to the non-inoculated rocks. The inoculated rocks were taken from an ongoing study of nutrient removal where an accumulation of microorganisms on the rocks was assured. Non-inoculated rocks refers to gravel as delivered. The reciprocation treatment refers to movement of water in the cells to facilitate oxygenation of gravel substratum. The parrot feather reactor systems (PF/D and PF/C) did not contain gravel and refer to parrot feather submerged in contaminated groundwater with or without nutrients.

Table 2.1

Treatment Identification Key.

Treatment identification	Parrot feather planted?	Rock status†	Carbon Added ?	Recipro-cation?	Description
CONT/C	no	none	no	no	Just water
CONT/D	no	none	yes	no	Just water
PF/C	yes	none	no	no	Parrot feather in water
PF/D	yes	none	yes	no	Parrot feather in water
YDN	yes	dirty	yes	no	gravel-based unit
NDN	no	dirty	yes	no	gravel-based unit
YCN	yes	clean	no	no	gravel-based unit
NCN	no	clean	no	no	gravel-based unit
YDY	yes	dirty	yes	yes	gravel-based unit
NDY	no	dirty	yes	yes	gravel-based unit
YCY	yes	clean	no	yes	gravel-based unit
NCY	no	clean	no	yes	gravel-based unit

† dirty = inoculated rocks, clean = non-inoculated rocks.

Nutrients were added to the contaminated groundwater as powdered milk at a concentration of 350 mg/L. The powdered milk contained 3.56% N, 0.75% P, and 0.8% Ca. Dissolving 350 mg/L resulted in nutrient concentrations of 12.5 mg/L N, 2.6 mg/L P, and 2.8 mg/L Ca in solution. A 350 mg/L solution had a chemical oxidation demand of approximately 420 mg/L and organic carbon concentration of 153 mg/L.

During the course of the study, water samples were taken for analysis of TNT, RDX, 2-aminodinitrotoluene (2A-DNT), and 4-aminodinitrotoluene (4A-DNT), using HPLC. Other water quality parameters measured were chemical oxygen demand (COD), redox, dissolved oxygen (DO), temperature, electrical conductivity, and pH. Redox was determined with an in-situ platinum electrode and a calomel reference electrode. Redox values reported were referenced to a H_2 reference electrode by adding 244 mV to the measured data. The average daytime water temperature, electrical conductivity, and pH were 24.7 (2.3) °C, 0.225 (0.129) mS/cm, and 7.12 (0.48), respectively, with standard deviations shown in parenthesis. Data presented in the following figures represents an average of 2 replications.

The decline in TNT and RDX concentrations were modeled by first-order kinetics. The linearized first-order kinetic model was used to determined the rate constant, K, from the slope:

$$\ln (Ao/A) = K\,t$$

where Ao is the initial concentration, A is the concentration at time t, K is the first order rate constant, and t is time. Units for time was days (d). Therefore, the unit for K is 1/d. The K constant is dependent on plant biomass concentration, as well as any other environmental factor influencing degradation. To analyze removal under varying plant biomass concentrations, Saunders et al. (pers. comm.) equates K to an second order rate constant (k) and plant concentration (PC) as:

$K = k\ (PC)$.

With PC in units of g/L, K in units of 1/d, and k having the units L/gd. "Little k", was determined from K for TNT degradation in our experimental units with parrot feather planted at 50 .

If K and Ao are known parameters and a target concentration of an explosive is given as A, the time needed to reduce the concentration from Ao to A is given by rearranging the linearized first-order equation above:

$t = \ln (Ao/A)/K$ = retention time in wetland system

Time (t) can be taken as the retention needed for reducing concentration of a compound from Ao to A when degradation occurs with rate constant K. Retention time and K are inversely related, the lower the K value the longer the retention time required. In bar graphs comparing the K constants for TNT and RDX removal with the various treatments, the retention time is plotted on the right y axis so a quick comparison of both rate constants and retention times can be made across treatments.

Tab for Section 3.0

SECTION 3.0

RESULTS

3.1 Impact on TNT Degradation

The inoculated (dirty) gravel systems (YDN and NDN) and the parrot feather system with carbon (PF/D) removed TNT quickly (Figure 3-1). TNT concentrations in these systems dropped below the detection limit after only 0.2 days (4 hours). The inoculated gravel systems with reciprocation (YDY and NDY) and the parrot feather system with carbon (PF/D) did nearly as well (Figures 3-1 and 3-2). Even the ponded water system with nutrients (CONT/D) was effective in reducing TNT concentration, albeit at slower rates than non-reciprocating (anaerobic) or parrot feather systems.

TNT removal in the inoculated non-reciprocating gravel systems (YDN and NDN) was believed to be due to anaerobic degradation since redox was less than -200 mV (Figure 3-3). Redox in all the other systems were generally greater than 100 mV (Figures 3-3 and 3-4).

Reciprocation had no effect on TNT removal in systems using uninoculated, or "clean", gravel. This can be seen via comparison of milk fed clean gravel systems without parrot feather (NCN versus NCY) in Figure 3-2; as well as by comparison of clean gravel systems with parrot feather (YCN versus YCY). Use of parrot feather did improve TNT degradation in the clean systems (compare NCN & NCY versus YCN & YCY) and reduced treatment time to non-detection levels by approximately 2 days.

The improvement in TNT degradation with planting ponded water with parrot feather was a little greater and may be due to greater surface area of plants exposed to water for exudation of nitroreductase enzyme (see comparison of ponded water without nutrient (CONT/C) and parrot feather without nutrient (PF/C) in Figure 3-1).

Among the gravel wetlands, the best at removing TNT from contaminated groundwater were those having inoculated rocks fed with nutrient solution (Figure 3-5). The carbon

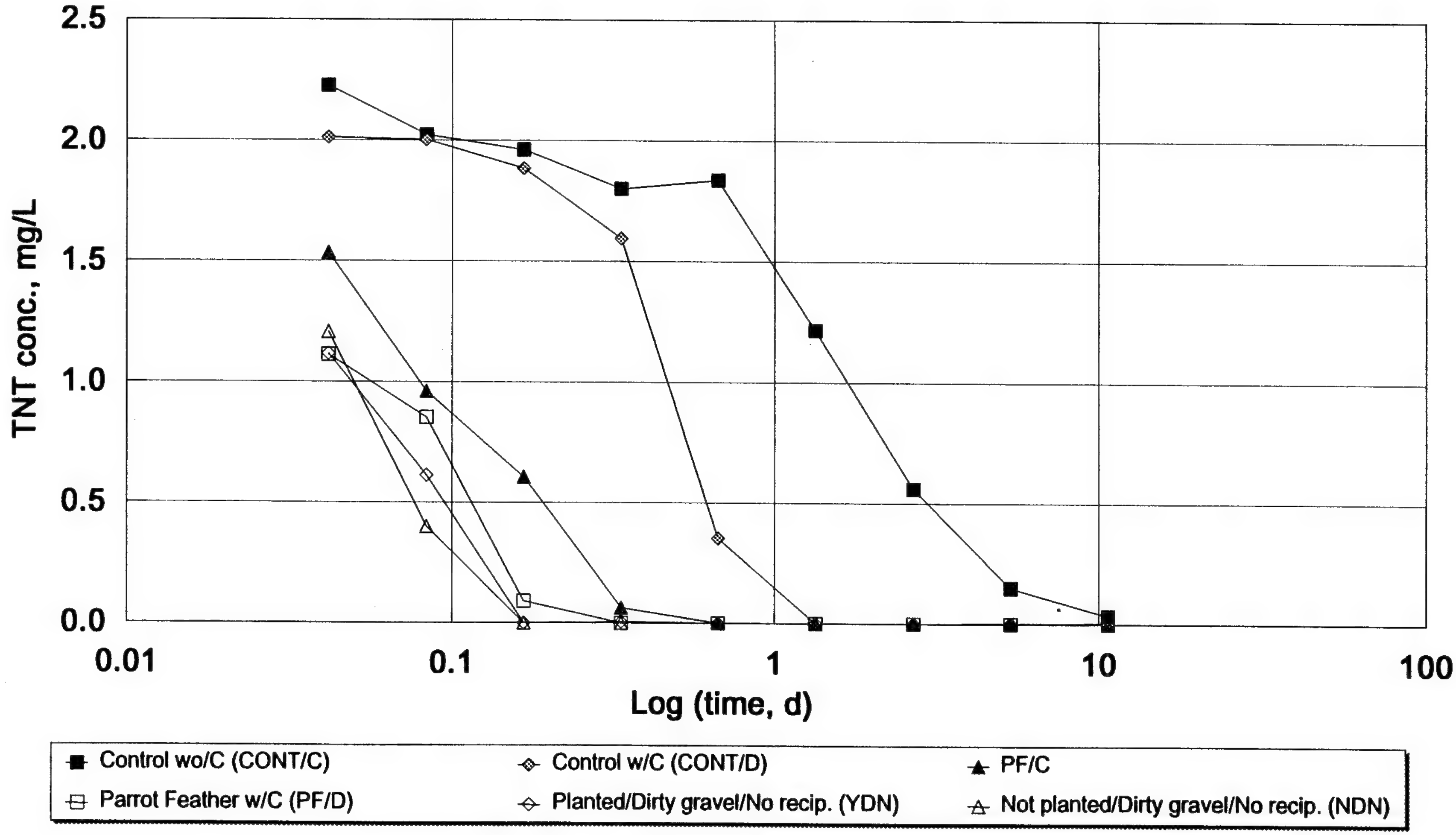

FIGURE 3-1
TNT REMOVAL IN GROUNDWATER

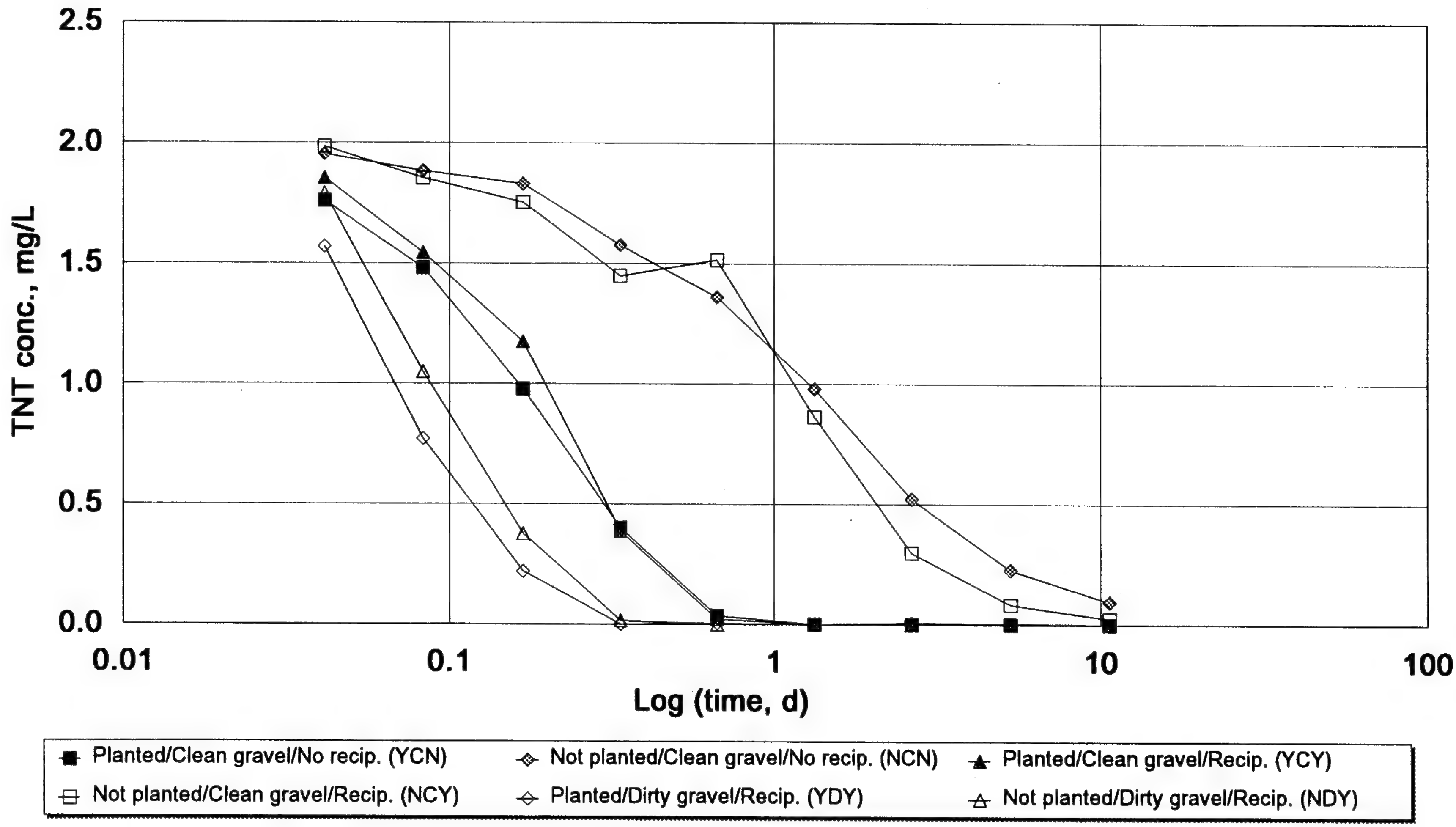

FIGURE 3.2
TNT REMOVAL IN GROUNDWATER (CONTINUED)

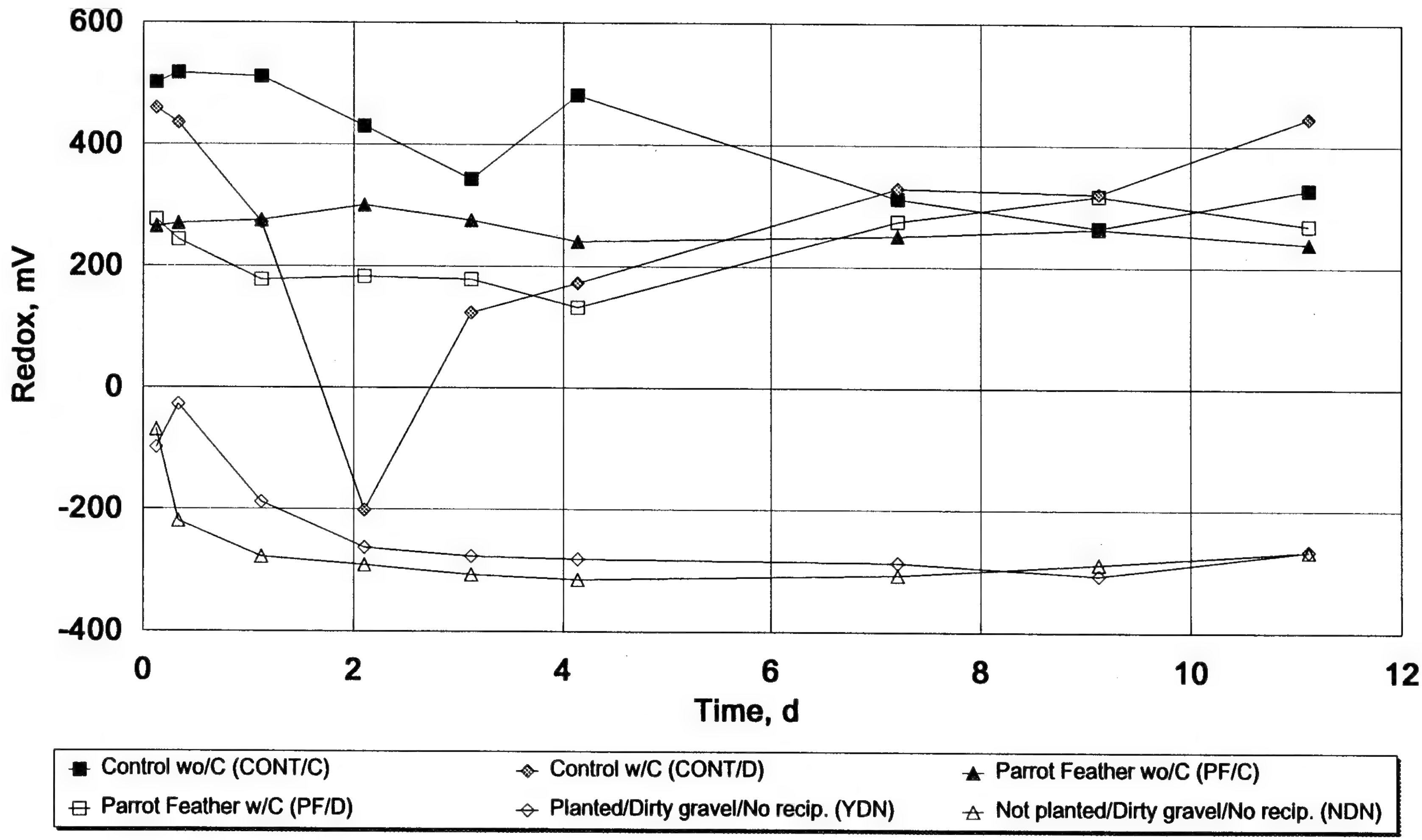

FIGURE 3-3
REDOX VALUES IN WATER

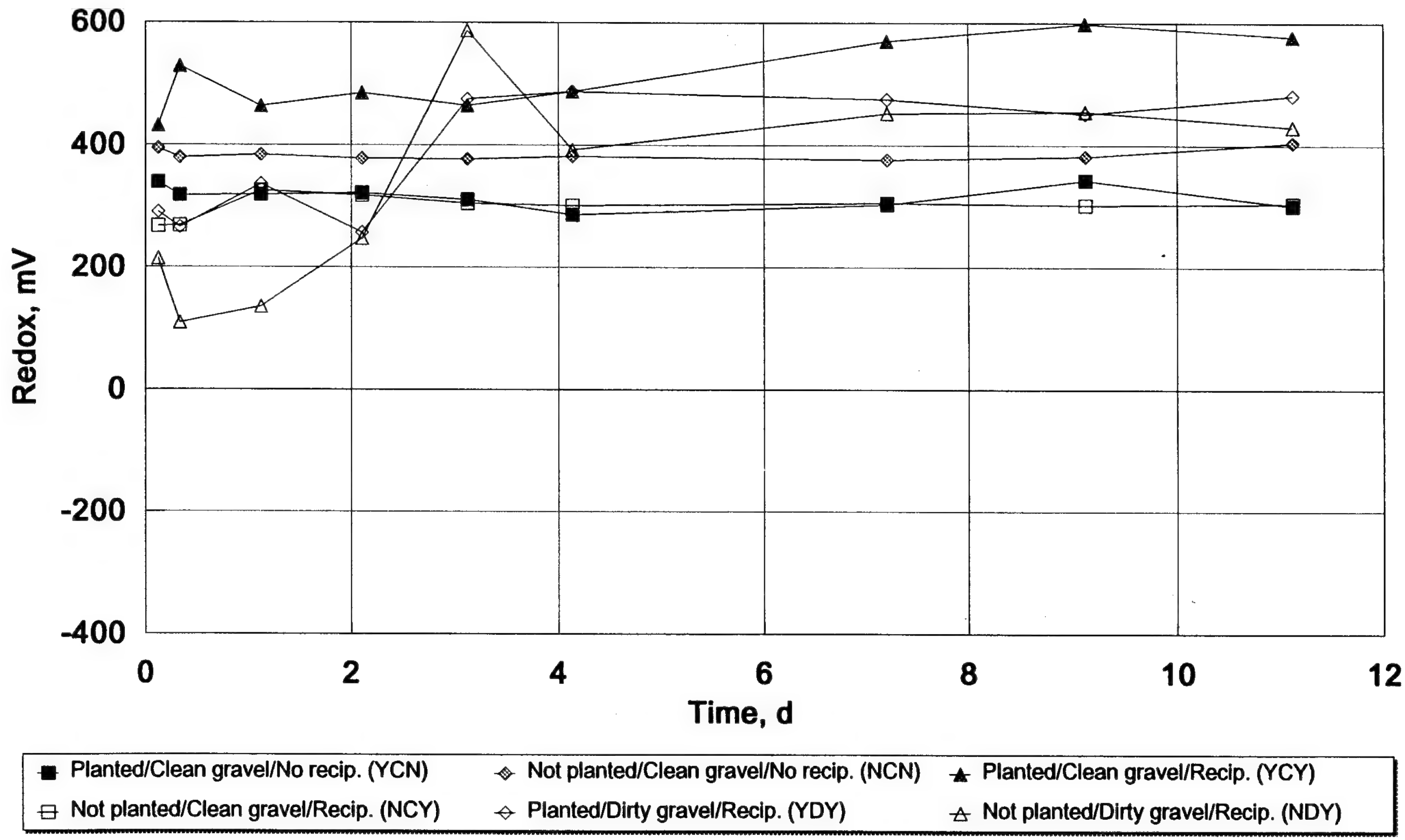

FIGURE 3-4
REDOX VALUES IN WATER (CONTINUED)

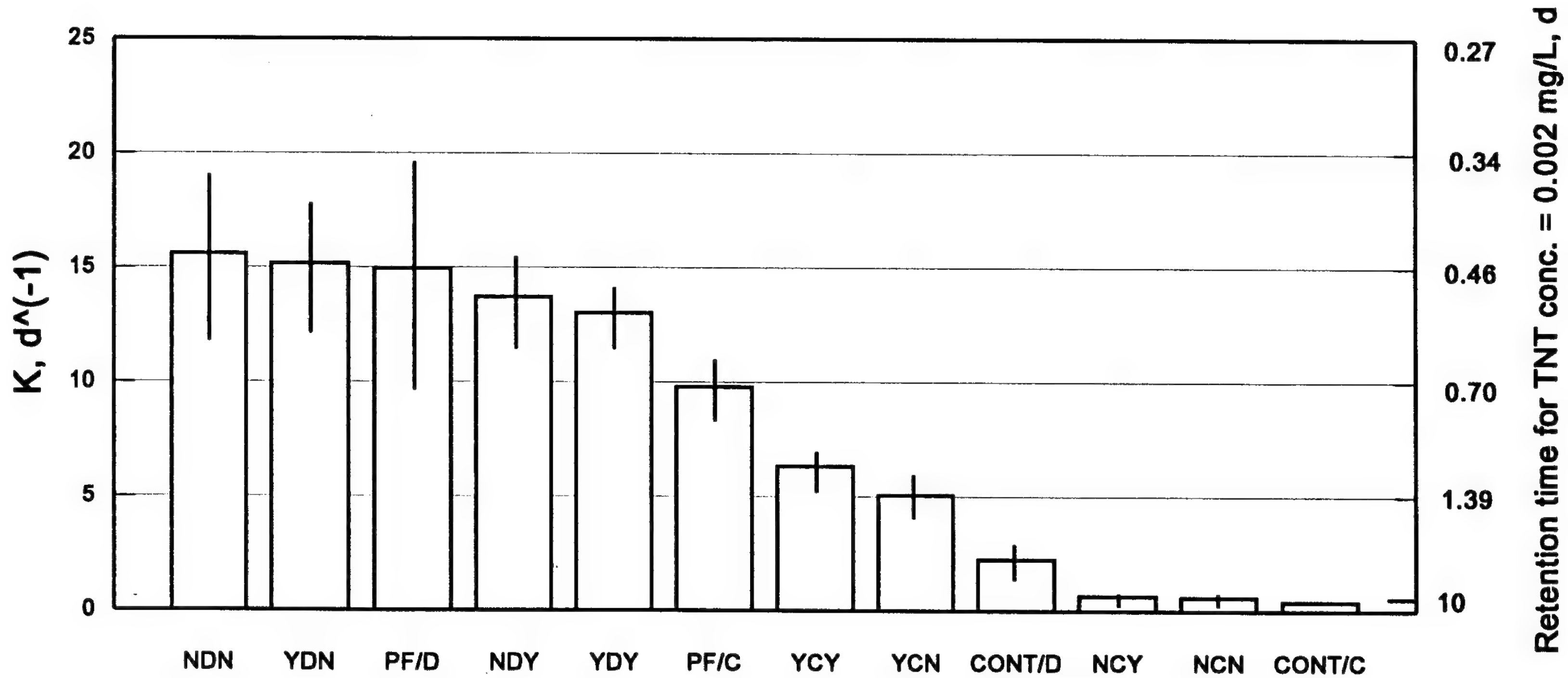

FIGURE 3-5
TNT REMOVAL RATE CONSTANTS AND RETENTION TIMES

present in the nutrient solution probably caused anaerobic conditions to develop with subsequent anaerobic degradation of TNT. When experimental error is taken into account, see bars in Figure 3-5, all treatment systems with added carbon had roughly the same impact on retention time whether or not the systems were reciprocating or planted with parrot feather. And this is true whether parrot feather is present or not. Retention times for adequate removal of TNT in the best systems ranged from 0.44 to 0.48 days. Adequate retention times for the parrot feather system without nutrients (PC/C) and all the clean gravel systems (YCY, YCN, NCY, and NCN) were significantly greater

"little k" constants were calculated for all TNT test systems containing parrot feather. The "little k" constant for YDN, YDY, PF/D, and PF/C were 0.30, 0.26, 0.29, and 0.20 L/gd, respectively.

3.2 Impact on RDX Degradation

RDX degradation occurred more slowly than TNT degradation as evidenced by higher retention times and lower K constants, see Figures 3-6, 3-7, and 3-8 respectively. The only gravel systems with appreciable RDX removal capability were the carbon fed non-reciprocating systems with inoculated gravel (YDN and NDN). Retention times required to lower RDX concentrations to 0.05 mg/L in these systems would be approximately 5-7 days (Figure 3-8). As with TNT, RDX removal was suspected to be due to anaerobic microbial degradation due to the redox levels <-200 mV in these treatments (Figure 3-2).

RDX degradation was observed in the nutrient fed parrot feather system as well. However, a retention time of 40 days would be required to make this system effective.

3.3 Degradation Product Levels

Degradation product levels were always less than 0.4 ppm (Figures 3-9, 3-10, 3-11, and 3-12). Concentrations of 2A-DNT peaked at approximately 0.5 days (Figs. 3-9 and 3-10) while 4A-DNT peaked at approximately 1-2 days (Figures 3-11 and 3-12).

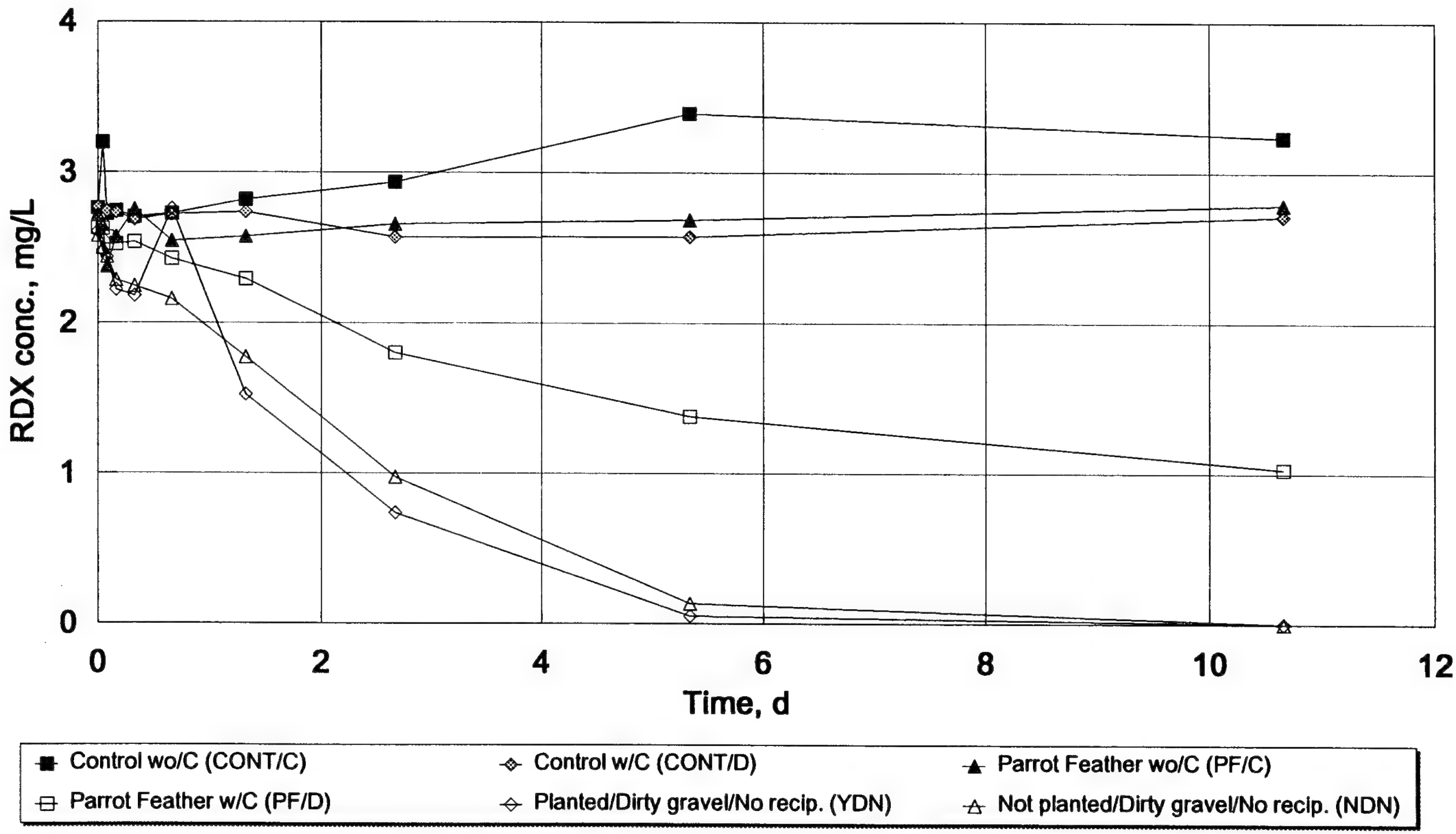

FIGURE 3-6
RDX REMOVAL IN GROUNDWATER

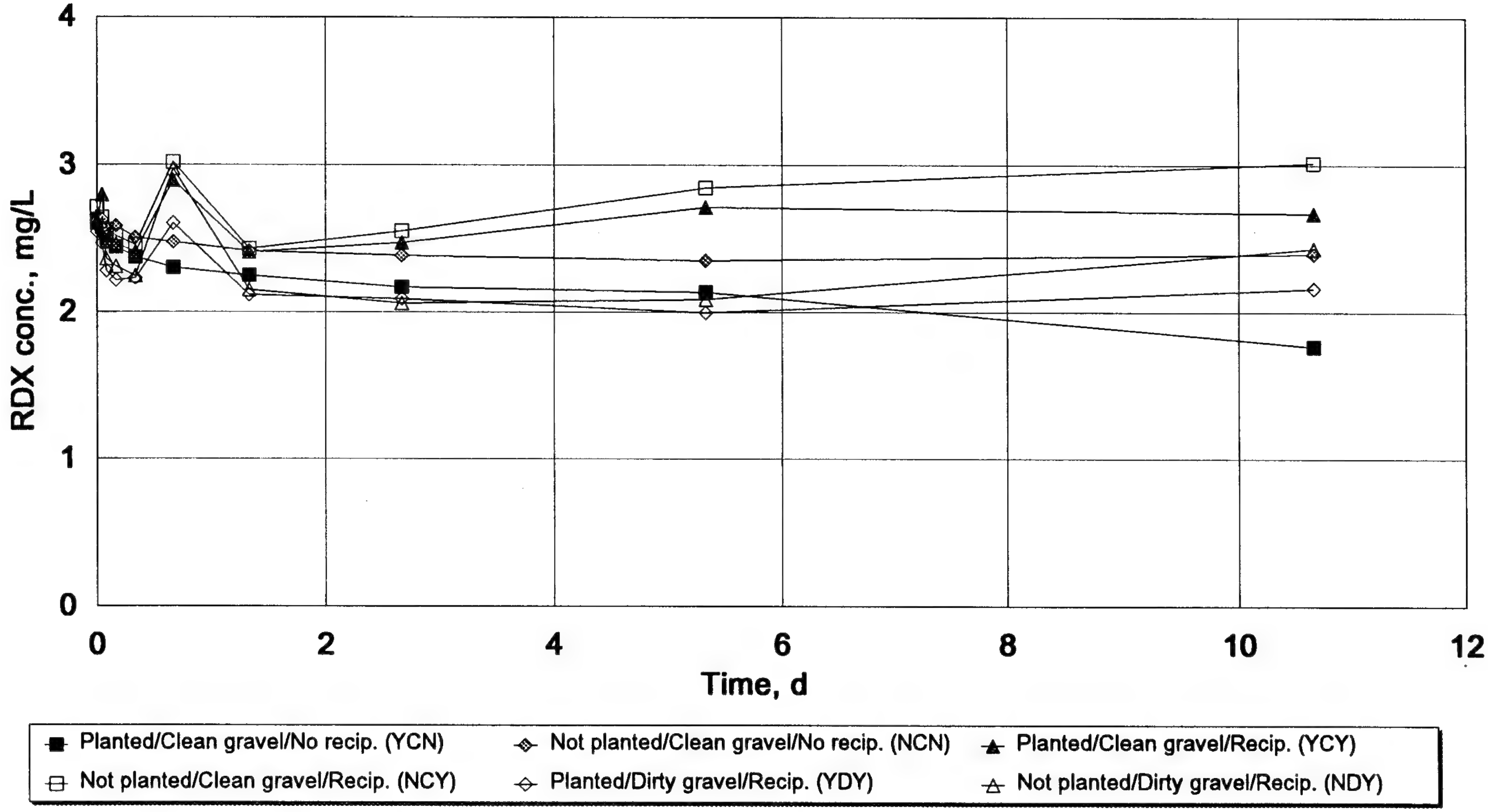

FIGURE 3-7
RDX REMOVAL IN GROUNDWATER (CONTINUED)

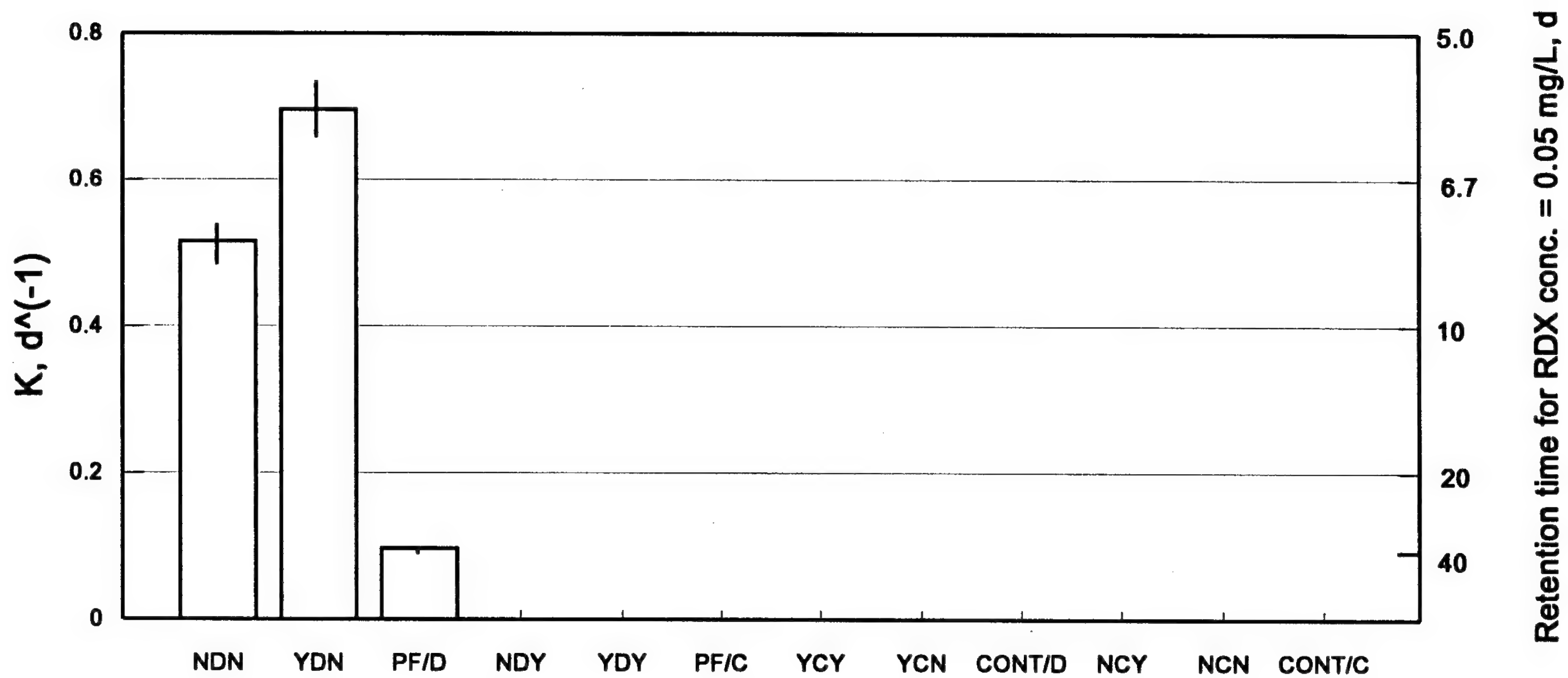

FIGURE 3-8
RDX REMOVAL RATE CONSTANTS AND RETENTION TIMES

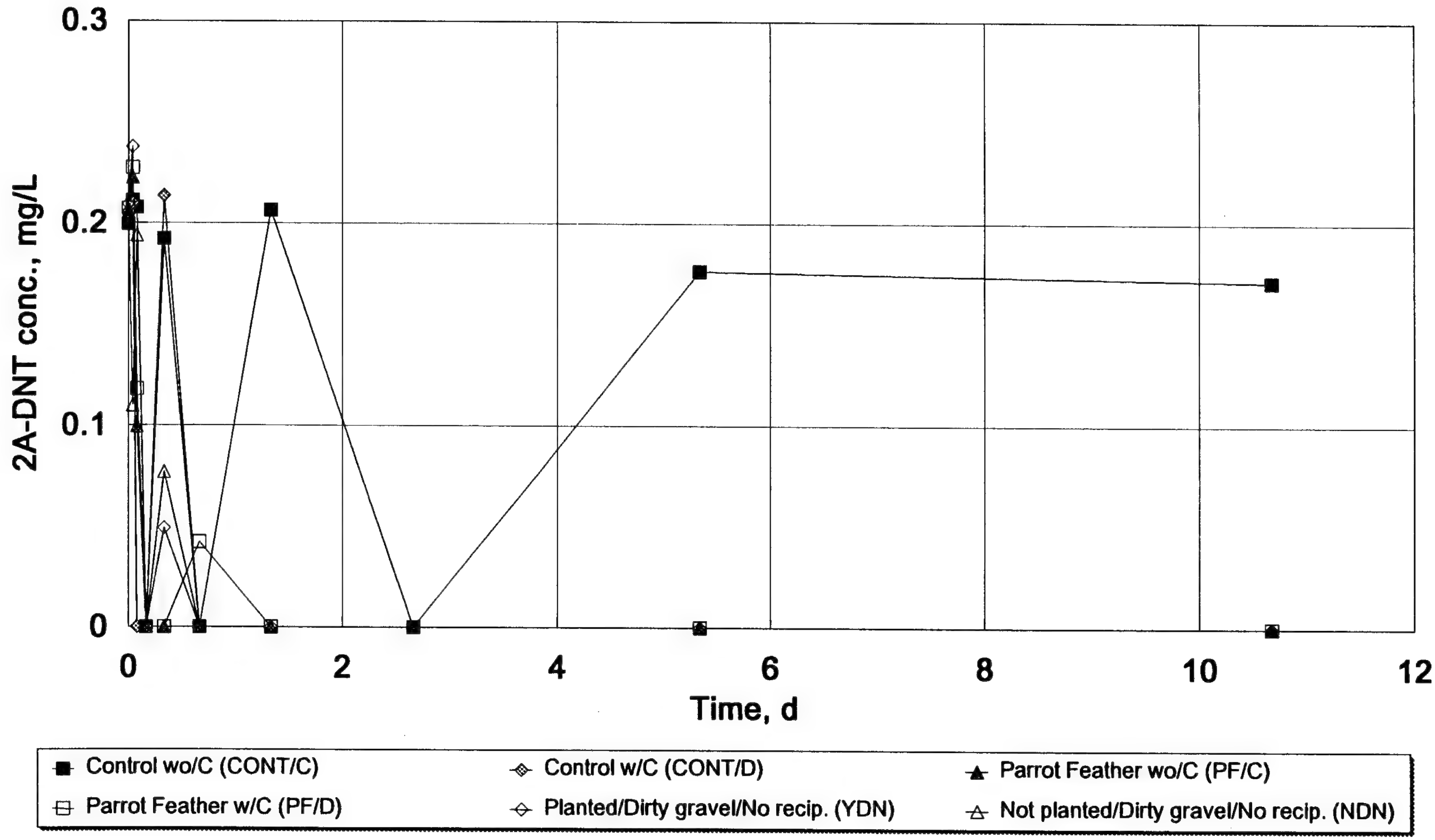

FIGURE 3-9
APPEARANCE OF 2A-DNT IN WATER

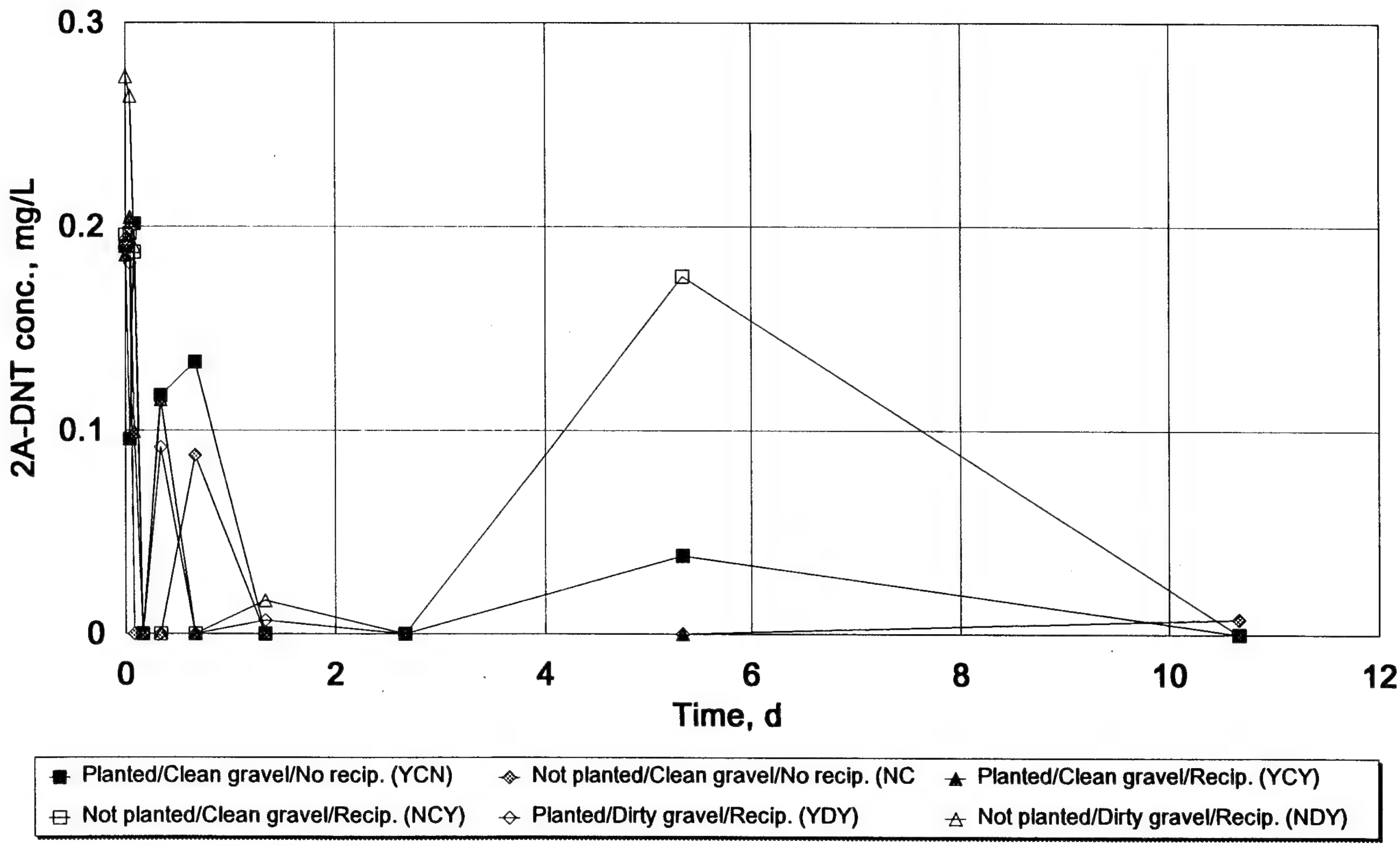

FIGURE 3-10
APPEARANCE OF 2A-DNT IN WATER (CONTINUED)

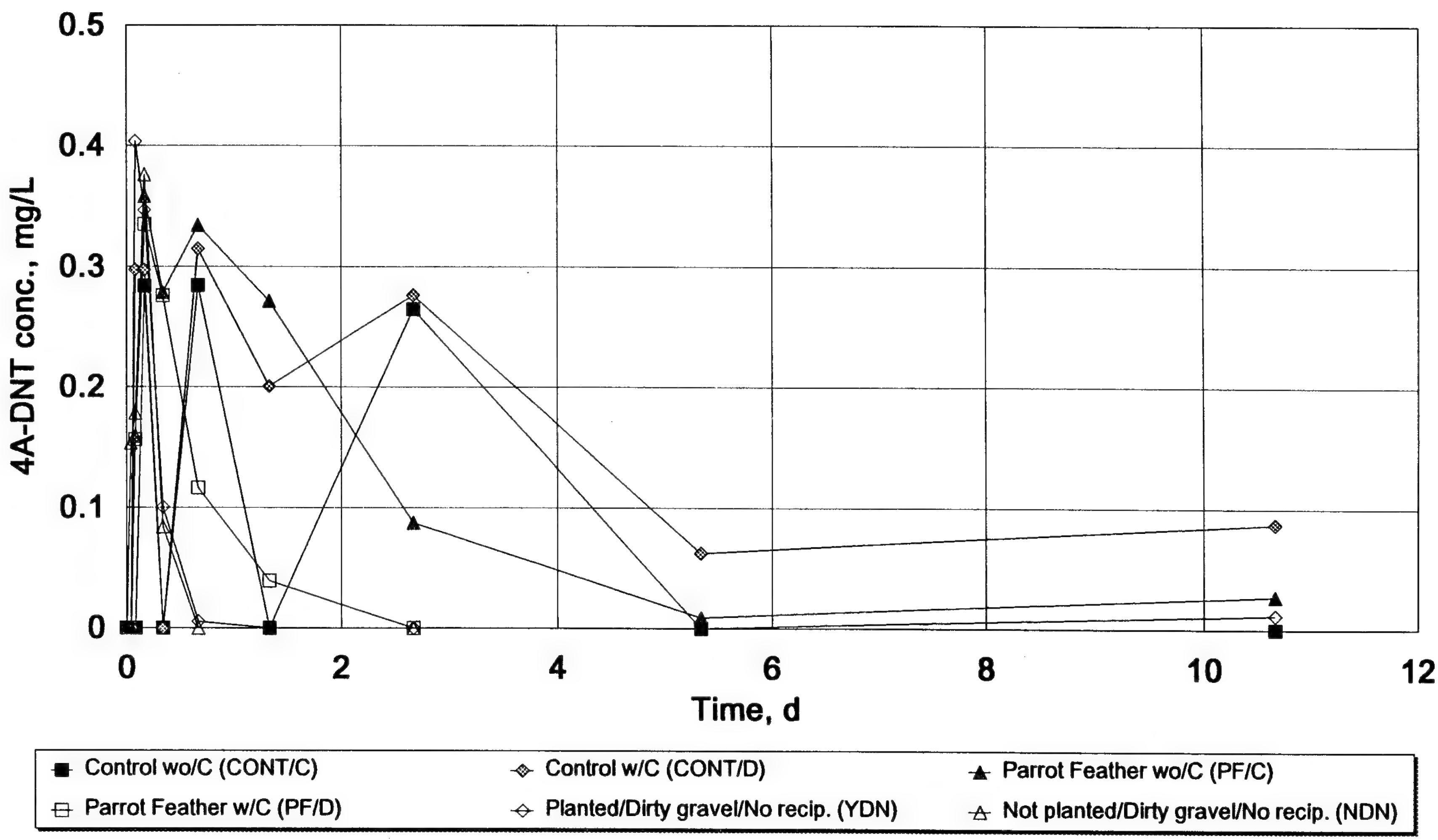

FIGURE 3-11
APPEARANCE OF 4A-DNT IN WATER

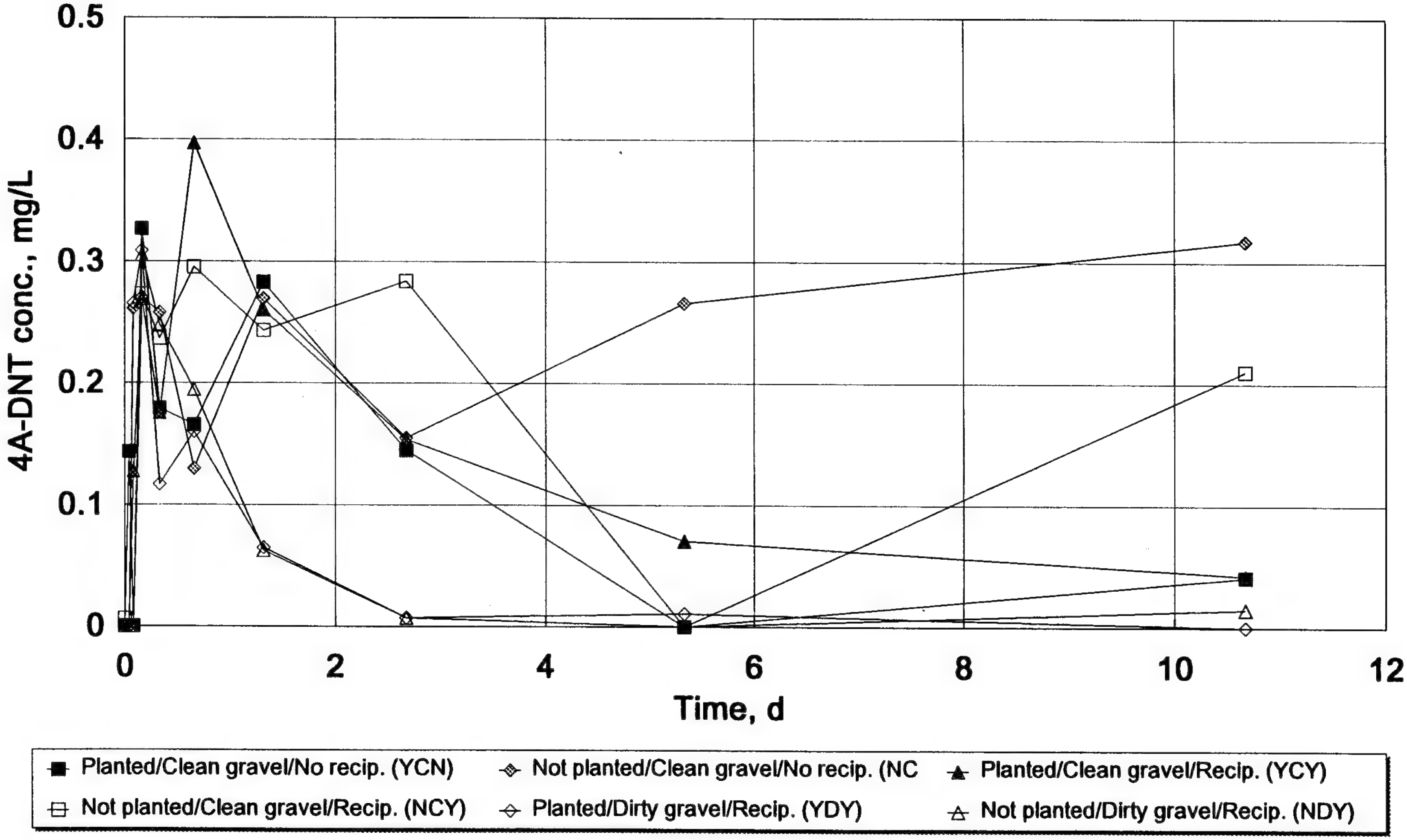

FIGURE 3-12
APPEARANCE OF 4A-DNT IN WATER (CONTINUED)

3.4 Impact on Chemical Oxygen Demand

Chemical oxidation demand is an approximate measure of the carbon content of water. The inoculated systems all had initially high COD due to the addition of the milk powder (Figures 3-13 and 3-14). However, the reciprocating systems were very effective in reducing COD in a very short time span (YDY and NDY in Figure 3-14). The parrot feather reactor without nutrients (PF/C) produced COD (Figure 3-13) probably due to organic exudates from plant roots. These results suggest that use of reciprocating wetlands could help control effluent COD levels by consuming residual carbon released from either parrot feather or anaerobic wetlands.

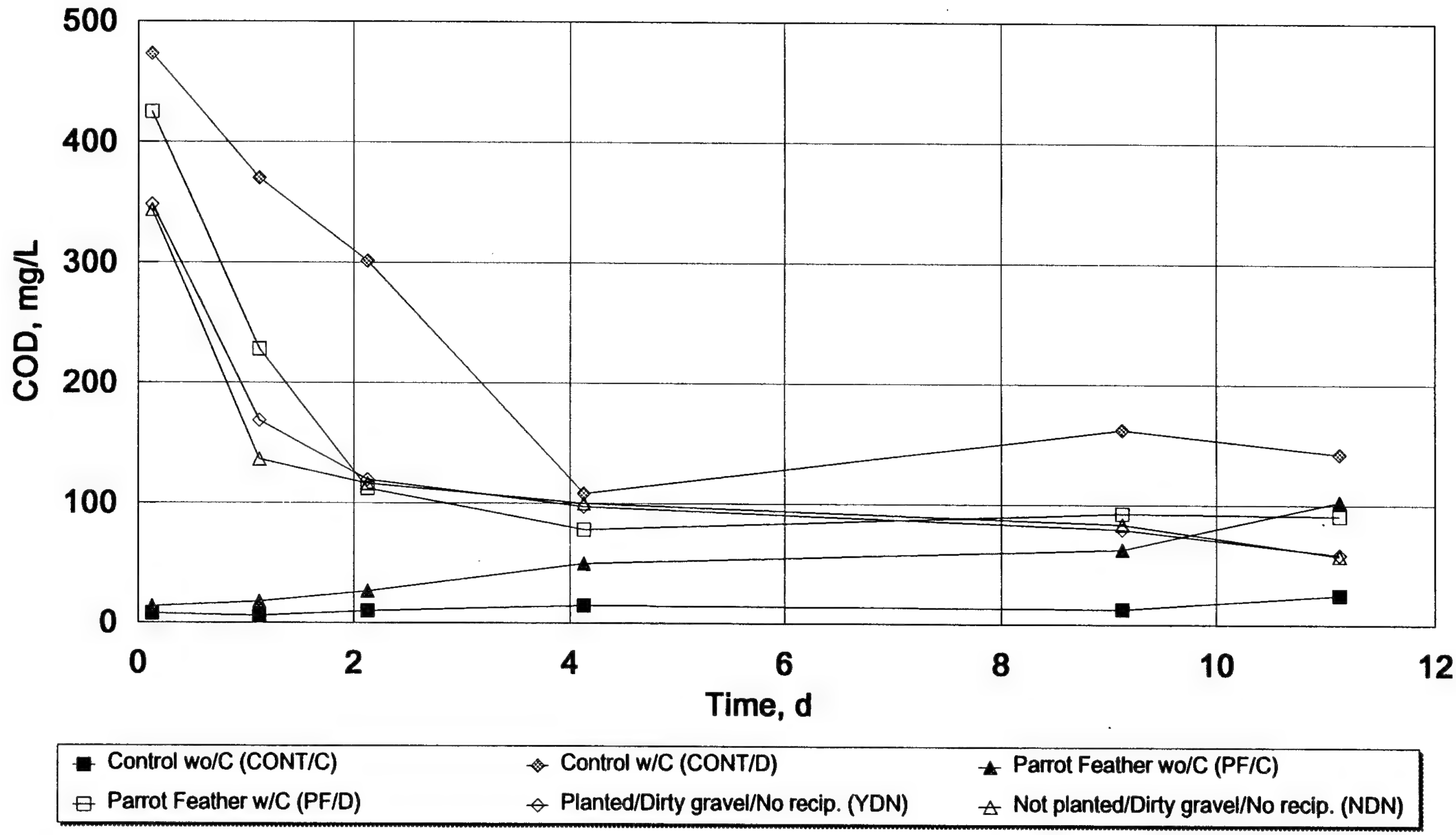

FIGURE 3-13
CHEMICAL OXYGEN DEMAND (COD) IN WATER

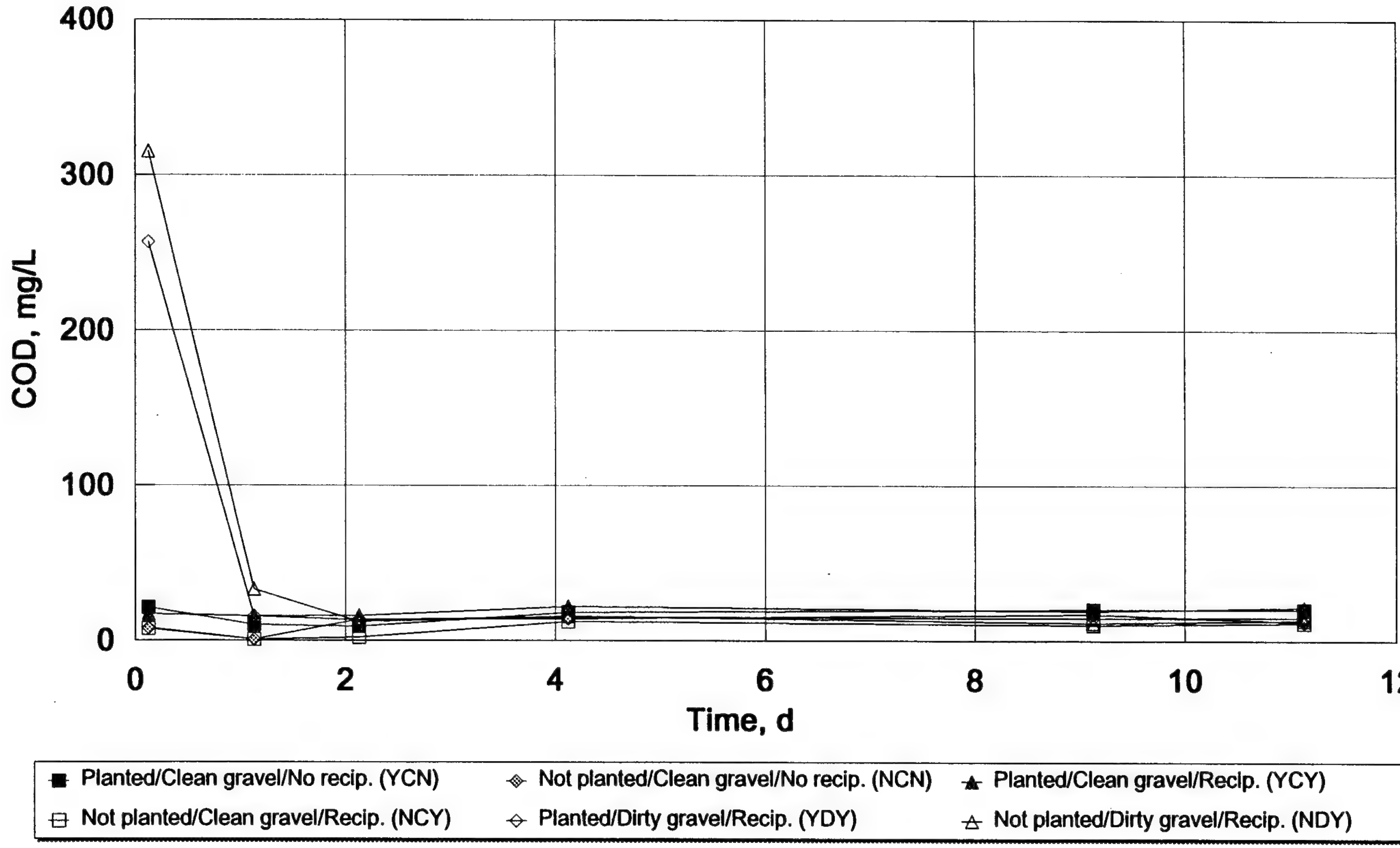

FIGURE 3-14
CHEMICAL OXYGEN DEMAND (COD) IN WATER (CONTINUED)

Tab for Section 4.0

SECTION 4.0

CONCLUSIONS

Anaerobic gravel-bed wetlands were as effective at removing TNT as ponded parrot feather systems. The removal of RDX was more effective in anaerobic gravel-bed wetlands compared to ponded parrot feather systems. Anaerobic microbial degradation was suspected to be the predominate mechanism for removal of TNT and RDX in the contaminated ground water. No differences in degradation products were observed among the treatment systems. These conclusions are important because, prior to this study, it was unclear whether gravel-based wetlands would degrade TNT and RDX in contaminated groundwater.

The study was also important as a basis for recommending design alternatives for the demonstration at Milan, Tennessee. The two systems recommended are a parrot feather reactor containing two cells and a gravel-based wetland containing two cells. With respect to the gravel-based system, the first cell should be designed for anaerobic degradation and the second cell should be modified to allow for reciprocation. Use of a reciprocating cell is recommended to quickly remove residual carbon and/or degradation products released from the first cell. According to the removal rates of TNT and RDX, the retention times for both systems should be approximately 8 to 10 days.

Tab for Section 5.0

SECTION 5.0

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